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A. P. Saab, L. N. Dinh

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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Andrew P. Saab and Long N. Dinh

Abstract

Diacetylene based hydrogen getters are examined in order to gauge their self decomposition products, as well as to determine possible origins for observed losses in getter capacity. Simple long term (several months) thermal aging tests were conducted, with periodic solid-phase micro-extraction (SPME) sampling followed by GC/MS analysis. The results suggest that bis(diphenylethynyl)benzene tends to decompose to give phenyl contaminants more readily than diphenylbutadiyne. Transmission electron microscopy (TEM) and electron diffraction studies of the palladium catalyst following varying extents of reaction with hydrogen show that there is no change to the catalyst particles, indicating that any change in capacity originates from other causes. These causes are suggested by Sievert's-type experiments on the reaction of the getter with a low pressure (about 10 Torr) hydrogen atmosphere. The reaction data indicate that the getter capacity depends on the pressure of hydrogen to which the material is exposed, and also its thermal history.

Introduction

Inhibiting metal corrosion by hydrogen gas can be achieved by the inclusion of a separate material with a high reaction affinity toward hydrogen. A common type of these hydrogen getters consist of a palladium nanoparticle catalyst supported on an amorphous carbon black, blended with a diacetylenic compound that irreversibly reacts with hydrogen. In typical studies, these materials are demonstrated to react vigorously with hydrogen gas. However, it is also commonly observed that the materials generally do not react to full theoretical capacity. At high hydrogen pressures without the benefit of cooling, the highly exothermic reaction can transform the material, which is usually tested as a fine powder, into a glassy substance. It is assumed that under such rapid

reaction conditions, the lost reaction capacity is due to material densification and pore obstruction caused by the intense heating. This in turn creates a hydrogen diffusion barrier, thus terminating further reaction at capacities many tens of percent below maximum.

However, most experiments run under more gentle thermal conditions still cannot ordinarily exceed about 90% capacity. One exception is described in a report from Kansas City Plant[1], wherein DSC experiments of small amounts of getter reacted in diluted hydrogen gas are determined to react to 99.5% capacity. However, the methods by which this figure is derived leave room for uncertainty about this value. The experiment does not take into account the appreciable volatility of DPB, which under even ambient temperatures can easily evaporate to skew apparent ratios of reacted to unreacted material. Also, the total heat evolved as determined by the DSC measurements was not compared to that predicted from theoretical calculations of the heat of reaction of DPB with hydrogen, which would have given a reasonable estimate of the actual percent reacted. Anecdotal reports of getter samples reacting with as little as 80% capacity abound, but little to no confirmation of these observations is available.

Another area of concern with getter materials is that of the decomposition of the getter to form benzyl species that can attack certain plastics used in deployment. Calculations show that this decomposition for DPB undergoing hydrogenation can occur with favorable energetics .

The present report examines the hydrogen getter with respect to both of these issues. Self-degradation is studied by subjecting gram amounts of getter to temperatures up to 70 ˚C, and sampling the headspace above the getter for analysis by GC/MS. The matter of capacity loss is evaluated from the perspective of physical and chemical alterations to the catalyst as a possible cause, and from that of early reaction conditions as determinants for the ultimate capacity of the material.

Experimental

Self-degradation

Stainless steel tubes fitted with SPME sampling ports (Figure 1) were loaded with glass vials containing 0.5 to 1.0 g of getter material, which comprised 75 wt% getter (either DPB or DEB) and 25 wt% catalyst (5 wt% Pd on C) . All getter materials were supplied by Kansas City Plant. As a control to account for any contaminant desorption from the catalyst, steel tubes containing only the carbon/Pd material were also prepared.

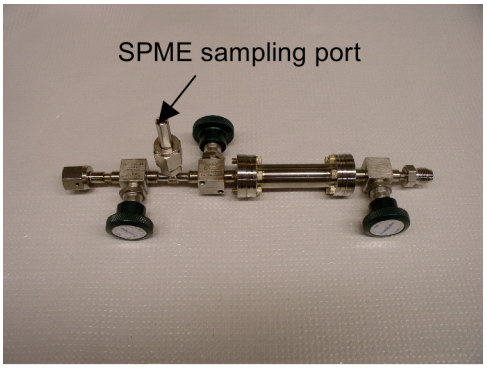

Figure 1. Sample tube for getter aging and SPME sampling

Initial SPME sampling was conducted at room temperature using a carboxin-PDMS fiber. Room temperature samples of pure DPB and DEB were also collected. The tubes were then placed into an oven at 70 ˚C, and allowed to remain for 1 to 2 months, during which time there were sampled for GC/MS analysis at random intervals.

Getter capacity

To evaluate whether or not changes to the catalyst were affecting the material reaction capacity, a reactor was constructed that would allow samples of the getter to be prepared to varying extents of hydrogen reaction. The device is illustrated in Figure 2. The pressure readout was set to control the solenoid valve in accordance with the pressures in both the inlet volume and the main vessel volume by connecting the internal relays of the controller in series. This enabled the controller to reach a broader overall pressure range than would have been possible with a single pressure input. At the minimum pressure, usually 1.00 Torr, the valve would activate, which would then permit pressurization of the inlet volume. By keeping the leak rate of the needle valve low, the internal pressure

of the inlet volume could reach a reliable maximum with only a slight error in the overall amount of gas delivered to the sample arising from the small amount of gas that leaked through the valve during the pressurization process. The gauges both had response times of milliseconds, ensuring that pressure tracking could be performed in real time. The volume of the inlet portion of the vessel was determined by computing the volume of the main chamber by direct measurement, then pressurizing the inlet space to a fixed pressure with the leak valve closed. After the pressure had stabilized, the valve was suddenly opened, and the system was allowed to come to a final pressure. The determined volumes were Vmain = 535 cc, and Vin = 8.1 cc. Several calibration runs of the equipment were performed. The error in the actual dose of gas delivered due to the leaking of hydrogen into the main chamber while the inlet volume was pressurizing was computed to be less than 4 %, based on the pressure measured in the main chamber at the same time as the peak pressure was reached in the inlet. An additional check of this was made by calculating the volume of the inlet space based given only the pressures at peak-time of the inlet vessel and the volume of the main vessel. This gave a volume of the inlet space of 8.3 cc, or about a 2 % error. This same volume was also calculated when the gas inlet process was run with the main vessel already containing 1 Torr of hydrogen, in reflection of the actual experimental conditions. This indicated that the flow rate of hydrogen from the inlet space into the main vessel was not measurably perturbed by the 1 Torr background. Thus, the accumulation of pressure in the inlet space would not be affected by the presence of gas in the main chamber. Further proof of this is performed by considering the flow regime of the setup.

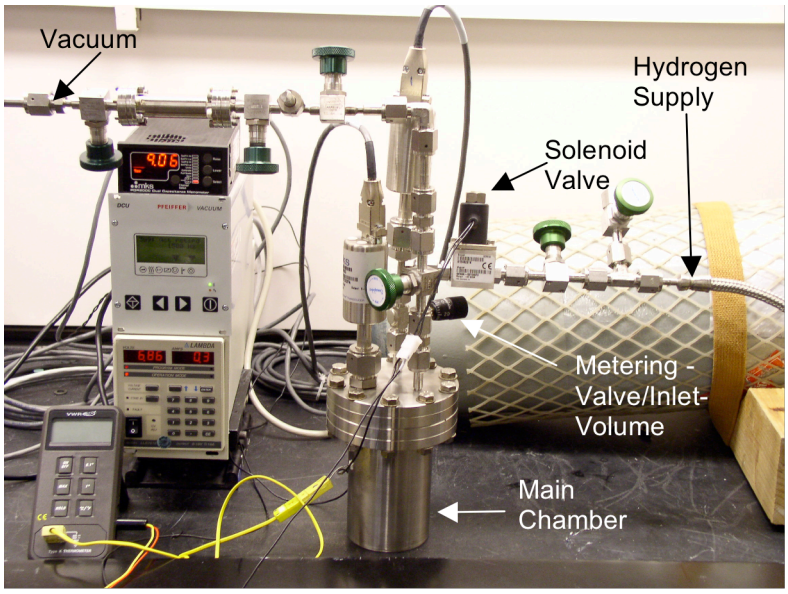

Figure 2. Hydrogen reactor apparatus

A large pressure drop across a small orifice will create sonic (i.e., choked) flow, that is independent of the downstream pressure, provided that:

$$\frac{P_{low}}{P_{high}} = \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma - 1}}$$

where γ is the specific heat ratio c_p/c_v of the gas. For hydrogen, choked flow will thus occur above an inlet-to-outlet pressure ratio of about 1.89. This is readily exceeded at most times throughout the experiment, thus the presence of background gas does not substantially affect the pressure building rate in the inlet volume when charging with H2.

Experiments were performed by placing a measured amount of getter material inside the main volume that would react fully with 10 inlet volumes of hydrogen at standard pressure. While DEB-based material would present no problems arising from volatility, DPB material could possibly have lost getter to sublimation, thus skewing the results. Other researchers have dealt with this either by calibrating their experiment to account for sublimed DPB, or by using a diluent gas meant to slow the sublimation of DPB by acting as a diffusion barrier. For the present work, the situation was handled by simply including in the vessel a bulk amount of DPB equal to about 20 times that which was contained in the getter material. Considering that the equilibrium vapor pressure of DPB has been measured to be about 10-4 Torr at room temperature, and that the volume of the entire apparatus is slightly greater than 500 mL, it is unlikely that significant loss of DPB occurred under these conditions.

Data were collected with a 16-bit DAC card on a PC. Typical scan rates were 1 Hz. Smoothing and averaging were performed after collection was completed.

Results

The typical amounts of simple phenyl contaminants as detected by SPME sampling and subsequent GC/MS analysis after two months of heating are presented in table 1. After several weeks of heating the getter/catalyst-blend materials, sampled headspaces showed a pronounced presence of benzene in the DEB samples. The DPB/catalyst samples were much less consistent, with only small amounts of either benzene or toluene detected in some samples. It is possible to attribute the presence of these compounds to materials other than the getters. Also present in all samples, and clearly confirmed by exact matches to NIST reference spectra, are several phenyl siloxanes. These contaminants probably emerge from the pumping system used for evacuation, or from an elastomer seal on one of the tube ports, or are present as a contaminant on the GC column. Assuming that they were contaminants in the actual vessel, it may be that the presence of phenyl compounds is due to their decomposition. However, these phenyl species were not present in samples of pure DEB and DPB, nor in the samples taken from pure Pd-on-C catalyst material. It is therefore quite likely that the phenyl products did emerge from decomposition of the getter.

Sample	Simple Aromatic Compounds/Max. Abundance
Pd/C Catalyst	None detected
DPB/Pd/C	Benzene*/1.5% Toluene*/2.5%
DEB/Pd/C	Benzene/29%

Table 1. Results of SPME/GC-MS analysis. Percentages are of ion chromatogram peak area to total ion chraomatogram area. (*) indicates not present in all samples

The carbon-supported catalyst introduced practically nothing above the normal background of the instrument. Likewise, direct sampling of both pure DPB and pure DEB indicate that the materials do not contain significant amounts of untoward aromatic substances, although it is significant that no parent peak for either DPB or DEB was detected. This indicates a very low affinity of these molecules for the carboxin-PDMS SPME fiber used for sampling. All samples showed a considerable amount of acetone, which probably originated from the sample vessel cleaning procedure.

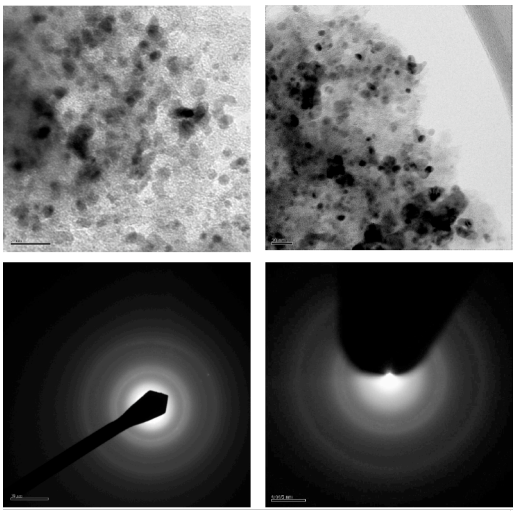

Figure 3. TEM micrographs of Pd-on-carbon catalyst (a) before and (b) after hydrogenation. The lower Figures show the beam diffraction results of individual Pd crystallites in the respective samples

Evaluation of the catalyst material by TEM was also performed, and these results are given in Figure 3. Figure 3a displays a TE micrograph of the catalyst prior to hydrogenation. The palladium particles are roughly 3-4 nm in diameter, and generally appear as darker spots against the lighter carbon matrix. Figures 3b and 3c show TE micrographs of the catalyst after it has been used in hydrogenation reactions of DPB and DEB, respectively. No changes to the catalyst size or distribution are evident. Likewise, electron diffractions of individual crystallites in the samples (lower portions of Figures 3 a and b) do not indicate any morphological changes to the catalyst particles.

The results of the time-dependent hydrogen pressure experiments are presented in Figures 4 - 7. In all cases, for both types of getter, the material kinetics slowed with each subsequent hydrogen dose, showing progressively slower drops in pressure. Also, midway through consumption of the ninth pressure charge, the reaction rate typically slowed and fell to near zero, corresponding to 80-85% consumed capacity after correcting for residual pressure and the precise amounts of gas in all administered pressure charges. Introduction of additional pressure up to 10 or 11 Torr would reinitiate the reaction, but only for another 2 or 3% consumption. For DPB samples, the rate slowed appreciably at long times following the first few doses. However, the pressure did not reach a steady-state during the first five or six pressure charges, indicating that at the time of dosing the reaction was still proceeding measurably, albeit slowly, when the next charge was introduced. In all cases the pressure drop did not follow an easily described functional form, such as a single exponential, reflective of the greater-than-first order kinetics of the reaction. Consequently, it was not possible to perform an empirical fit with a common function that is well behaved beyond the bounds of the data, and that

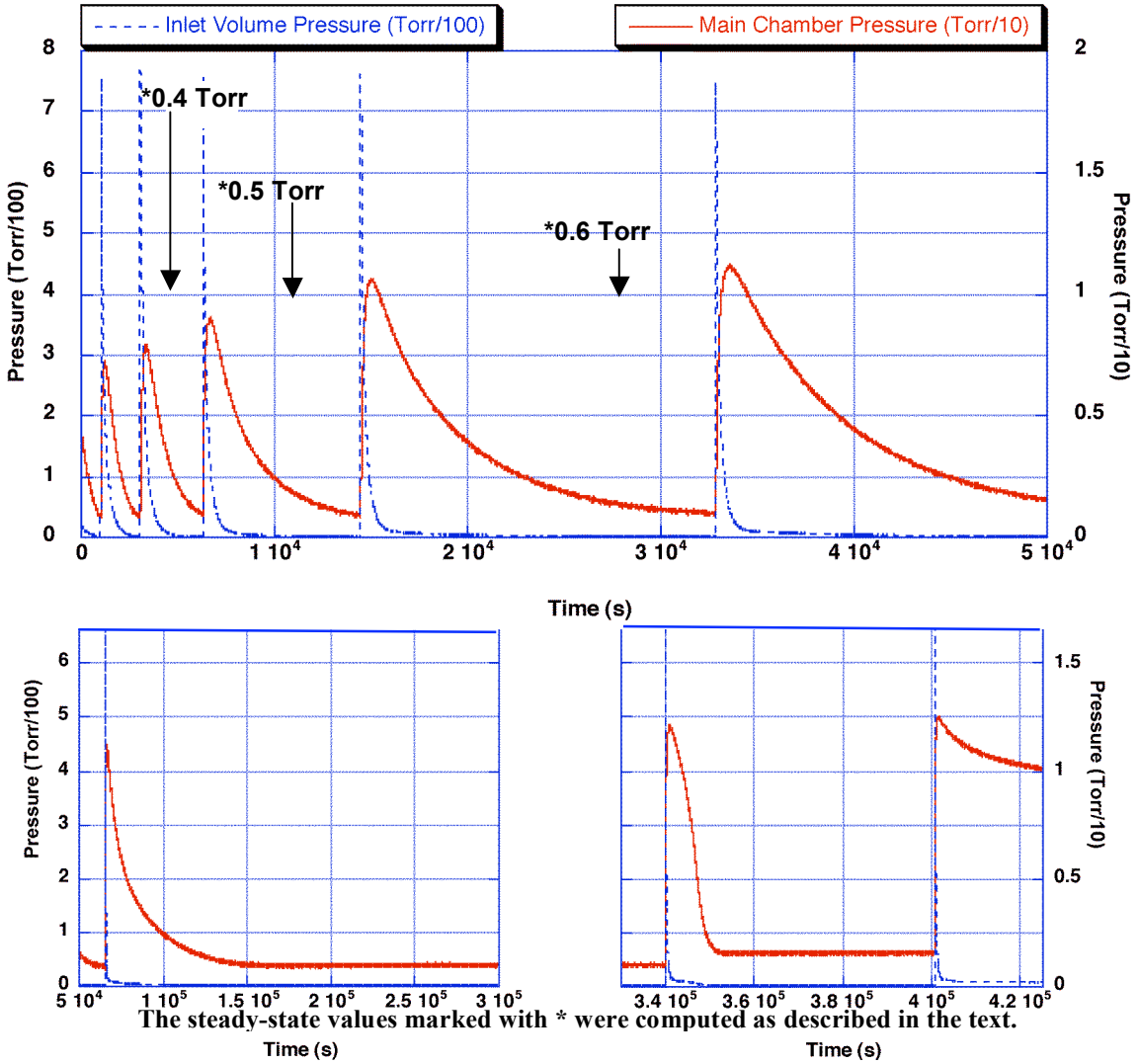

Figure 4. P vs. t for typical DPB/Pd/C

would consequently allow for a prediction of the asymptotic value of the pressure for these first few hydrogen doses. However, it was possible to create an estimate of the long-term behavior by considering a plot of the time needed to consume 10% of the hydrogen remaining at any time (perhaps best considered as a "0.1 life", in analogy to a half-life). For example, a plot of these values taken from the segment in Figure 4 spanning 7500 s to 15000 s clearly shows a decelerating behavior, Figure 5. This indicates that the reaction at these intermediate points in the experiment would never approach zero, but rather some finite value, if the experiment was left undisturbed and no additional hydrogen dose was applied. The plot fitted well to an

exponential at long times, so was used to predict the 0.1 time at long intervals. Since over short time spans (on the order of a thousand seconds) the actual data does fit well to a single exponential, it is possible to consider the reaction to be pseudo-first-order over these periods. Consequently, the 0.1 time can be used like a half-life to predict a dummy value of the rate constant *k* over these spans. A plot of k vs. time in thousand second intervals is presented in Figure 5. The synthesized *k* values further indicate that the approximation is justified since *k* changes only by a few percent from one thousand-second interval to the next at most. Then, using the integrated rate law for a first order reaction and the last value of pressure at the end of a given pressure segment, the value of P at the end of the subsequent thousand second span was calculated. This value was then used as the initial pressure for the computation of pressure after the next thousand seconds, and so on. For the present case, a computer program was written to process the data. The results for intermediate pressure segments of the DPB experiment are presented in Figure 4 as asterisked values, showing that by the time intermediate capacities of the getter have been reached the system will come to a steady state pressure on the order of 1 Torr of hydrogen and react no further.

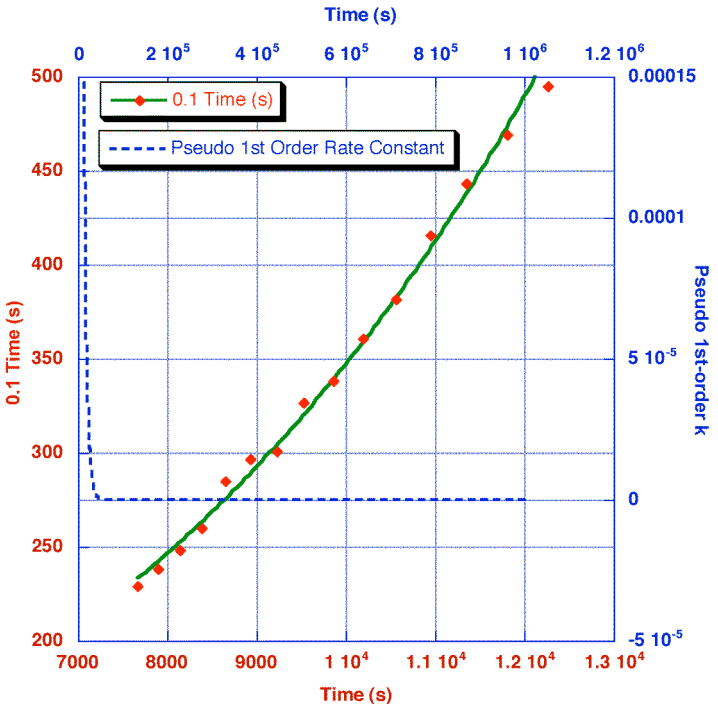

Figure 5. 0.1 time vs. time (red diamonds) with accompanying exponential fit (green curve), and predicted values of first-order *k* for one-thousand second intervals.

For DEB, the situation depends on the rate of admission of the hydrogen dose: for the faster rate used (the metering valve at the maximum adjusted setting) the behavior is nearly identical to that of DPB, with earlier reaction cycles following a continuous decay to the switching pressure (Figure 6). For the slower rate, the pressure decay after the

third reaction cycle is not monotonic, but instead undergoes a visible inflection to an entirely static regime where the pressure does not drop, Figure 7. Also, the amount of pressure accumulation was not consistent between DEB samples. In one case, after about

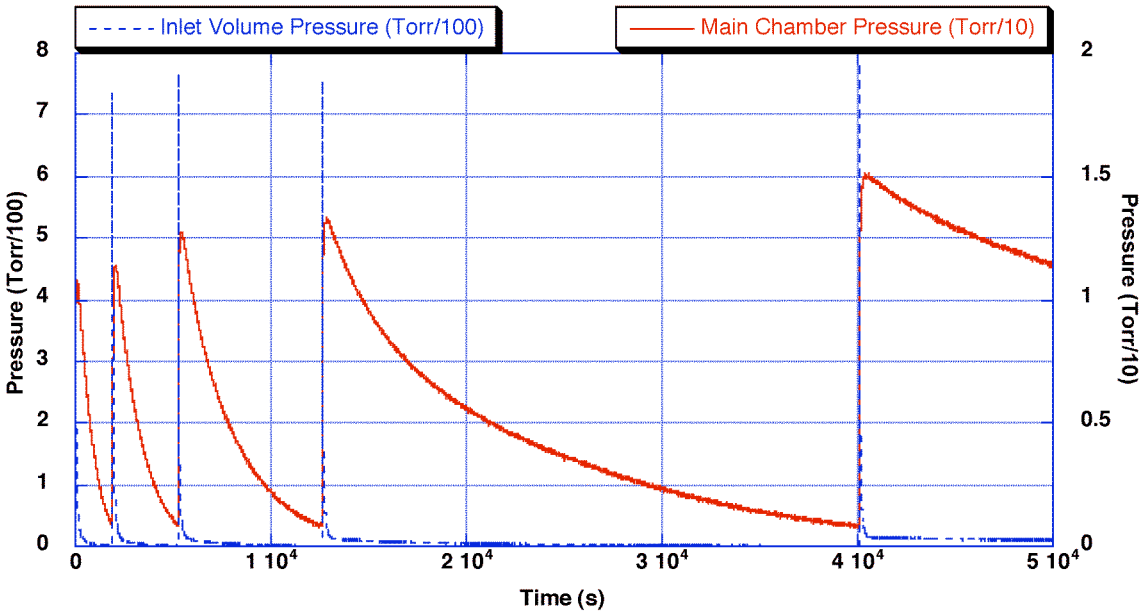

Figure 6. P vs. t for a DEB getter sample at a relatively fast hydrogen inlet rate

50% of reacted capacity had been reached, the remaining pressure was on the order of 1.5 Torr. For another sample, not shown, the remaining pressure was about 0.5 Torr, even though the trend behavior was identical to that of the other DEB sample. These samples were identical in all terms, except for the ambient temperature. Maintenance of the laboratory's ventilation system in the interval between these experiments raised the mean temperature from about 16 ˚C to about 20 ˚C for the two samples, respectively.

Discussion

The most intriguing part of the reported data is the P(t) reaction experiment. The general trend among these data is that as the level of getter consumption increases, the background hydrogen pressure that the material can tolerate with little or no apparent reaction also increases. Further, after about 75% of the material has been reacted at these low pressures, subsequent exposure to pressures of about 10 Torr of hydrogen produced a reaction substantially slower than the rates presented at earlier times.

These data indicate that a getter uptake experiment that is performed by reacting getter material with a single large volume of hydrogen at low pressure (within the envelope of the current experiments, about 5 Torr or less) can lead to a situational estimate of the

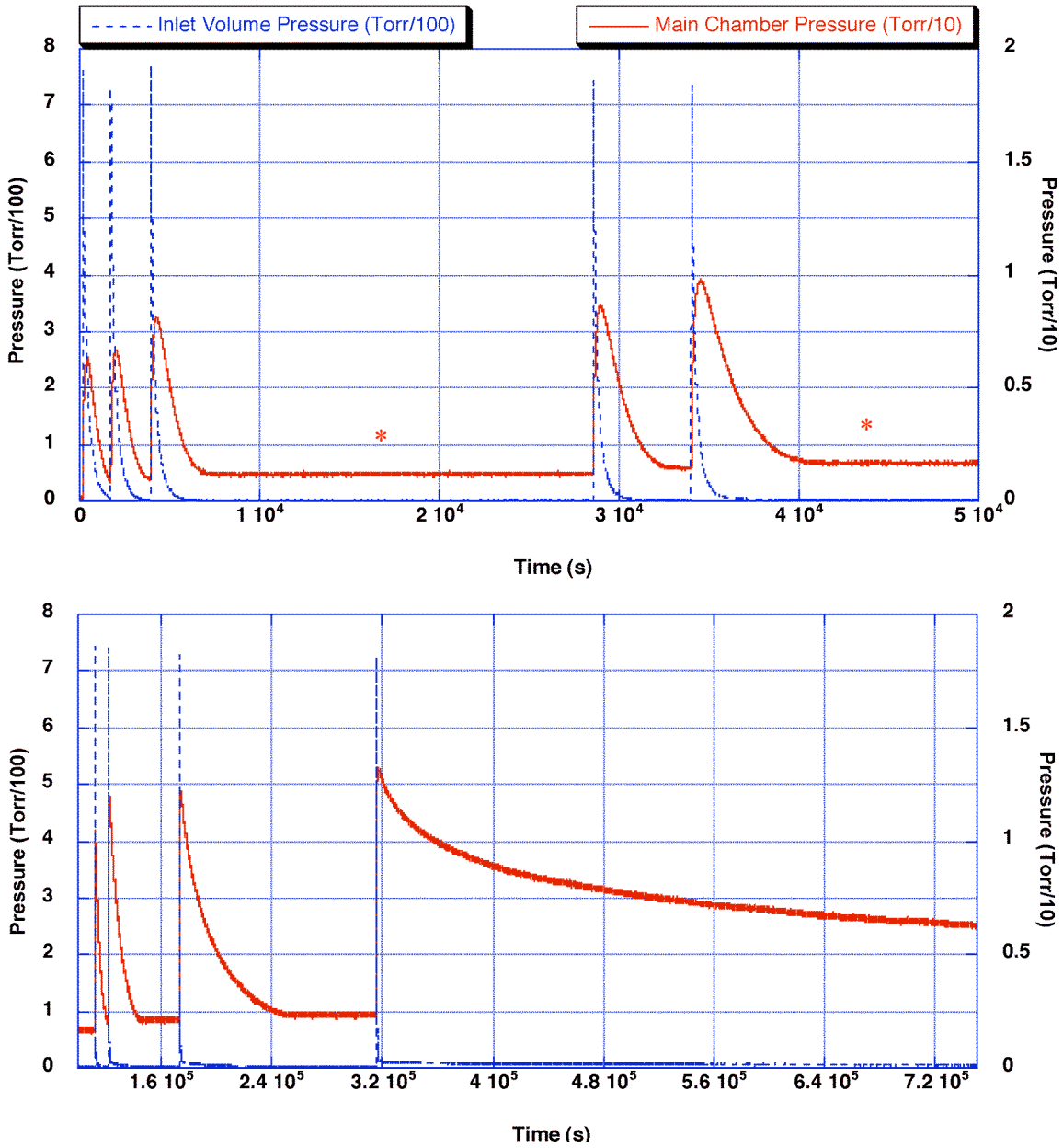

Figure 7. P vs. t for a DEB getter sample at a relatively slow hydrogen inlet rate. The final steady state value of about 6 Torr was observed after several days. Increasing the pressure artificially to roughly 11 Torr induced about 2 to 3% additional reaction.

getter capacity. For example, an experiment beginning with a static high-volume charge

of gas near 5 Torr, and expected to approach 0.5 Torr after completion would probably show rate behavior above 75% capacity very similar to that displayed in the present data. The result would be an estimate of capacity of the getter of about 80%, since the reaction would seem to shut off at this level of consumption. Likewise, for experiments conducted at lower pressures, the earlier plateaus would suggest that the capacity could be estimated as being correspondingly lower, anywhere from 40% to 60%.

Thus, attempting to gauge getter uptake capacity with low pressure large volumes of hydrogen could lead to diminished capacities as has been anecdotally reported. However, as shown by the data in this report, if the pressure is artificially raised by further addition of hydrogen gas, the capacity will increase.

In order to properly assess capacity as a function of pressure, it is required to react the sample in a pressure cell with a proportional feedback of hydrogen input that maintains a constant pressure by matching the inflow rate with the gas depletion rate due to reaction. In this kind of experiment, the hydrogen activity remains essentially fixed, which will allow the actual reaction rate and the true getter capacity to be measured as a function of applied hydrogen pressure. This experiment has the distinct advantage of allowing for valid kinetic measurements to be gathered, since only the getter compound activity changes in this case. It also allows for the apparatus to remain compact, since a large ballast volume is not needed to approximate a fixed activity.

It is necessary to address the possibility that the accumulation of pressure in the chamber was not due to remaining hydrogen, but rather to the formation of volatile decomposition products resulting from the hydrogenation. As described above, the SPME results indicated that even in the absence of hydrogenation, the getter was undergoing some decomposition to form volatile phenyl compounds in the presence of the catalyst. The addition of a vigorous reaction such as the hydrogenation might serve to enhance this decomposition. Yet, it must be noted that the partial pressures of hydrogen and the decomposition product resulting from reaction are inversely proportional to each other, and should stand in an approximately fixed stoichiometric ratio. In this case, a fixed

decrease in hydrogen pressure should result in a more or less fixed increase in partial pressure of organic volatiles, assuming that the reactants and products are roughly the same throughout the entire reaction profile. The data indicate that the increase in the pressure background does not proceed by fixed increments after consumption of equivalent hydrogen doses. In fact, the difference in the subsequent increases can be several tens of percent, up to nearly double what would be expected from one dose to the next. If due to accumulation of volatiles under the conditions stated, this would suggest large variable changes in the hydrogen consumption during various reaction cycles. Also, the equilibrium vapor pressure for fully hydrogenated getter compounds has been measured to be no more than 10^{-3} Torr at room temperature[3], well below the measurement limit of the apparatus. Thus, it is likely that a significant portion of the accumulating gas is hydrogen.

There are some interesting differences between the behavior of the DPB and DEB materials. While the inlet rate of hydrogen seems to have no impact on DPB samples, DEB samples show a change from monotonic pressure decrease to a decrease with an inflection (see Figures 6 and 7) beginning with early reaction cycles. There is no evident cause for this behavior. Another difference noted that is specific to the DPB sample that produced the data in Figure 4 is the oddly shaped pressure curve beginning near 3.4 x 105 seconds. The origin of the obviously accelerated behavior of this reaction segment is unclear, but may be related to an apparent dependence of reaction rate on time elapsed between reaction segments. This effect will be detailed below, in the context of the sample reaction mechanism.

The present data cannot be easily analyzed to give direct kinetic information. This is because the hydrogen pressure and the activity of getter with respect to the catalyst both change in time. Data relevant to kinetics would require one of these terms to remain fixed. However, it is possible, based on the observed trends to hypothesize about the mechanism at work that results in a reaction capacity dependent upon sample history.

There are two aspects of the data that are relevant in the context of capacity loss: first, the resumption of the reaction upon increase of pressure after the reaction has apparently stopped; and second, the difference in the apparent reaction rates as a function of time between successive hydrogen additions.

The first issue is particularly important in the context of the DEB materials subjected to lower hydrogen inflow rates. As noted above, for DPB, and DEB under faster inlet rates, the pressure profiles do not come to steady state within the measured reaction times. They do slow substantially, however, and the data are predicted (values marked * in Figure 4) to come to steady state at longer times.

In contrast, for DEB under low inlet rates, the data clearly show that the reaction simply shuts off beginning with early reaction cycles, with the pressure drop undergoing a discontinuous transition to zero rate of change. Yet a subsequent hydrogen addition at relatively higher pressure reinitiates the reaction. This could be attributed to a certain initiation pressure needed to begin the reaction, but this is not consistent with the known behavior of virgin getter material reacting immediately with low hydrogen pressures; neither is it consistent with the fact that the getter reduction is an essentially irreversible process. However, it is consistent with a gas breakthrough phenomenon arising from accumulation of hydrogenated getter material that acts as a gas diffusion barrier. It has been previously observed that reacted getter material appears to be imbibed with liquid, which is presumably related to the hydrogenated diacetylene. This same observation was made in the present experiments, particularly with intermediately reacted samples, which seemed much like an inky slurry. Such a material could fill pores and void spaces that otherwise serve as diffusion pathways of the hydrogen to the catalyst.

The second noteworthy behavior, that of the time dependence of the apparent reaction rate on delay time between hydrogen additions, is best considered in view of the mass transport properties of the reactants in the hydrogen/palladium/getter-molecule system. Theoretical calculations[2] show that for this system, a reactive complex does not form involving any of the three species. Instead, hydrogen readily forms radicals on the Pd

surface, which are then highly mobile, and which react directly with an acetylene bond when encountered. Consequently, the fundamental requirement for reaction in this system is one hydrogen radical in close proximity to one unsaturated bond.

This requirement is deceptive in its simplicity. For the classic case of heterogeneous catalysis in a liquid, relatively rapid mass transport by liquid diffusion and convection can allow for very high conversion rates of the relevant substrate even if the substrate and catalyst are separated by a large distance on average. However, the present system is not a bulk liquid. Given that the Pd is present at 5 wt% with an average particle size of about 40 Å, and taking the carbon support to have a mean BET surface area of 200 m^2/g surface area (a typical value for Cabot XC-72 amorphous carbon decorated with platinum), the calculated nearest neighbor distance for Pd particles on a square grid is over 1100 Å. The high resolution TEM images in Figure 8 gives some indication of the actual separation of Pd particles on the carbon support. Because the support has a highly irregular surface, it is difficult to identify the actual mean linear distance from one Pd particle to another. However, the high resolution images identify those particles that are at the focal plane of the instrument, which are the particles that display clear crystal planes. In contrast, particles away from the focal plane appear less distinctly and show no crystal planes. Thus, the linear separation of particles at about the same height gives an idea of distances that separate nearest neighbor Pd particles. From Figure 8, the values range from what appears to be close-packing to more than 150 Å. The close packing, which is also visible in the lower resolution TEM images as large clumps, suggests the presence of significant

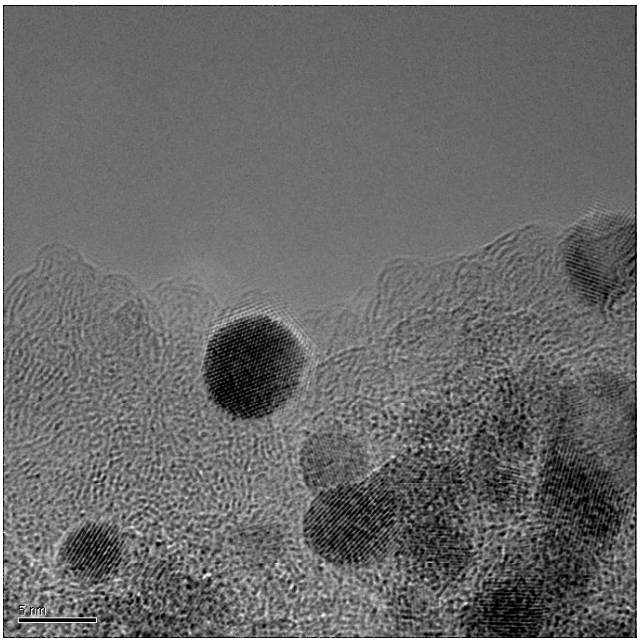

Figure 8. High resolution TEM image of Pd on C. The particles displaying crystal surface structure, which appears as ruled lines across the particle, are at approximately the same height in the frame of reference of the instrument. The scale legend corresponds to 5 nm.

areas of the carbon surface where the catalyst density is low. Taken in combination with the very high molar ratio of diacetylene compound to catalyst, this indicates that some of the getter must reside in areas with virtually no catalyst, and also in an appreciably thick layer above the Pd particles. A simple calculation that assumes DPB at an estimated density of 1 g/cm^3 dispersed with full density over a carbon substrate of about 200 m^2/g surface area at a mass ratio of 3(DPB):1(Pd/C) shows that the thickness of the DPB overlayer is on the order of 1μm. For the real material it will probably be on average thicker than this, since it is unlikely that all of the carbon surface area is accessed and uniformly wetted by the getter compound. Given the basic requirement for reaction stated above, the question then becomes, how is it that getter molecules residing so far from a catalyst surface can react to any great extent? The axiomatic answer is that either (a) getter diffuses toward the catalyst, or (b) hydrogen radicals leave the catalyst and diffuse to the getter.

Both of these possibilities present their own difficulties. Recent calculations[4] indicate that the removal of a single hydrogen radical from a Pd surface is exceedingly costly in energy. To better approximate the real situation, the calculation was also performed in the presence of benzene rings. The rings were added to investigate the possibility that the getter material itself supports H transport away from the Pd. Though there is a lowering of the energy cost in this arrangement, it is still prohibitively high. We have not yet examined the effect of the carbon substrate, but such calculations are planned. Regarding diffusion of the getter to the catalyst, the chief issue is the anticipated low mobility of large DPB and DEB molecules in the solid state.

Still, since at least one of these processes must occur, it is instructive to consider the various possible experimental results that could emerge from each limiting case, and to compare them with the actual data. Each case will be defined before comparisons are made.

I. Mobile getter / immobile hydrogen

The first limiting case is that for which all hydrogen mobility is limited to the surface of the catalyst, and only the getter molecule may freely diffuse. This results in the overall process being diffusion controlled with respect to the getter activity (proportional to concentration along an axis perpendicular to the catalyst surface). Under these conditions, an initial charge of hydrogen will react much as observed, with a resulting monotonic pressure decay. As a result of the initial reaction, an activity gradient of getter molecule forms. Once the gradient is established, mass transport of the getter at a distance from the catalyst toward the catalyst begins. For a relatively slow rate of transport, successive charges of hydrogen react more slowly than the last, as the gradient smears out and spreads farther into the region away from the catalyst (i.e., the diffusion is behaving semi-infinitely with a transmissive boundary condition). The reaction will proceed, more and more slowly, until the gradient is essentially gone, and only Brownian motion can drive any further reaction. At this point, the reaction can be taken to have come to completion, although it will still continue very slowly. The most notable consequence of this mechanism is that the change in the rate of the reaction from one aliquot of hydrogen to the next should depend on the amount of time that lapses between them. This is because the accumulation of fresh getter near the catalyst is itself a function of time. Therefore, allowing more time to pass between one charge and the next permits more getter to diffuse closer to the catalyst surface. The result is then a slower decrease in the reaction rate from one hydrogen charge to the next as a function of time between charges.

II. Mobile hydrogen / immobile getter

The second limiting case posits that dissociated hydrogen at the palladium surface can freely diffuse away from the catalyst to continue to react with immobile getter molecules at a distance. In principle, this mechanism should be indistinguishable from that of the diffusing getter case just on the basis of the apparent change in pressure. Put another way, the functional forms for the two processes should be very similar. However, there

should be one critical difference, namely that there should be little or no time dependence of the rate of change of the reaction rate between successive aliquots of hydrogen. For the case of hydrogen atom diffusion, after the reaction has slowed to the point that the hydrogen pressure is at or near steady-state, the activity of hydrogen atoms near the front of unreacted getter must either be constant or decreasing. As time passes, ongoing diffusion will continue to smear and flatten out the hydrogen atom distribution, causing the activity to further diminish below its value at the point where the reaction stopped. Consequently, a long delay after a hydrogen addition will result in a state of minimal activity of the hydrogen atoms in the vicinity of the getter. The result is that long lapses of time do not serve to enhance the reaction rate for a subsequent addition of hydrogen

Because the time-dependent pressure in the main chamber will result from a convolution of the rate of gas flow into the vessel and the rate of gas withdrawal due to reaction, the time value of the peak pressure in the main chamber (relative to the pulse initiation) gives an indication of the reaction rate for a given reaction cycle provided the inlet flow is constant. The decay of pressure in the inlet volume illustrates that for most hydrogen charges the inlet flow rate is nearly identical for all pressures in the inlet volume down to about 10 Torr. Thus, for peaks in main chamber pressure that occur before the inlet volume has reached 10 Torr, the reciprocal of the peak time is

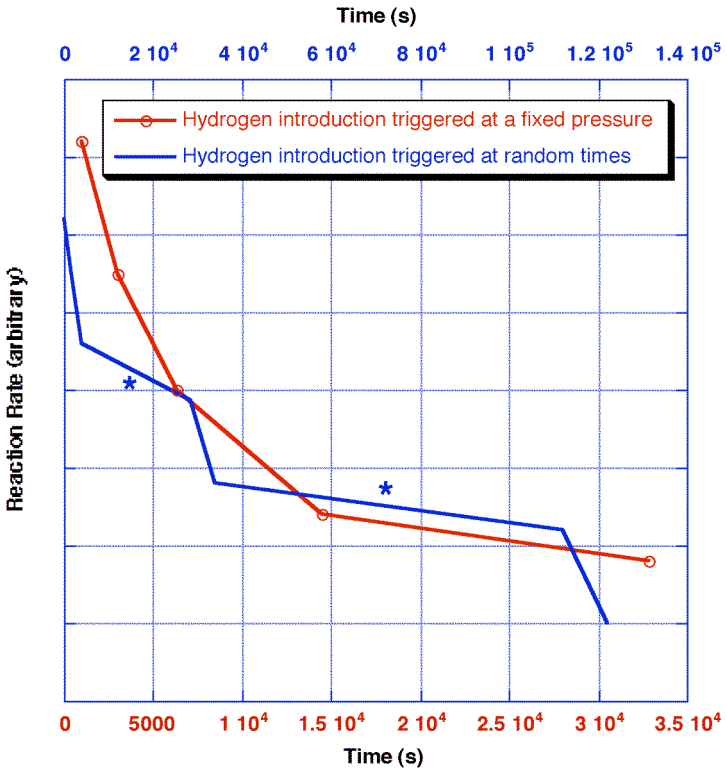

Figure 9. Reaction rate as a function of time for a sample with hydrogen introduction triggered at a fixed pressure (red) and for a sample with hydrogen introduction at random times (blue). The time intervals marked with * correspond to the intervals similarly marked in Figure 7.

directly proportional to the reaction rate. Figure 9 presents a plot of reciprocal peak time against the absolute initiation time of the hydrogen charges. Clearly, the reaction rate depends on the time elapsed before a given hydrogen addition: longer waiting times between additions will cause the reaction rate to increase disproportionately. This behavior is consistent with that proposed in the foregoing for the case of getter material diffusing toward the catalyst particles.

It is conceivable that the increase in reaction rate after a long period of time is due in some part to volatilization of reacted getter product that is otherwise obstructing gas access. If this were the case, then allowing the material to remain at steady state for a sufficiently long time should allow the reaction to reinitiate in the background of unreacted hydrogen remaining in the vessel. Though this was not observed, it is possible that times longer than those permitted during the experiments are required for this effect to manifest. In any case, it will be necessary to explore this mechanism as a contributor to the observed behavior.

The reported results and the above discussion allow for the formation of a hypothetical cause of reduction in getter capacity. The chief difference between samples that have been observed to react to 90% or more of capacity, and those described herein, is the rate of reaction, and therefore the rate and degree of heat evolution in the systems. In the context of getter diffusion being a controlling factor in the net kinetics of the hydrogenation reaction, increases in temperature can be expected to accelerate this diffusion and thus increase the amount of getter available for reaction at any given time. Consequently, it is possible that the heat generated by the reaction itself can feedback into the reaction kinetics by accelerating the getter diffusion. This is consistent with higher capacity being reported for cases in which the reaction proceeds more vigorously. Unless sufficient rate, and therefore energy, exists to ensure an adequate amount of getter diffuses close to the surface of the catalyst, the reaction shuts itself off or dwindles to a very slow rate. A further possibility in this framework is that the observed loss of capacity due to reacting a sample of getter very rapidly with a large amount of hydrogen could be explained in terms of the considerable heat evolved in a short time. This could

result in sublimation of both getter and the getter hydrogenate, thereby creating a wide depletion layer of reactant around the catalyst that cannot be replenished. Thus, a more complete description would be that neither too much, nor too little, thermal energy delivered in time is desirable in order to optimize getter capacity.

In addition to heat, there may be a solubility factor that impacts getter diffusion. It has been observed anecdotally that after full reaction pellets of DPB getter appear to soften. As noted above, getter material seems to liquefy to some extent during hydrogenation. If a liquid-like product exists during the course of the reaction, it could facilitate diffusion of the unreacted getter by dissolving it, thus providing higher mobility for the getter than a strictly solid process. However, it must also be considered that the presence of a liquid-like phase could negatively impact the reaction rate by forming a barrier to molecular hydrogen diffusion at low pressures.

Irrespective of the foregoing conjecture, the clearly non-trivial nature of the observed behavior suggests that the actual mechanism of getter reaction in these systems is more complicated than has been previously assumed, and warrants detailed controlled study of these phenomena. In any event, the results reported herein indicate that the loss of capacity in diacetylenic hydrogen getter materials apparently occurs under conditions of relatively slow reaction.

Conclusions and future work

The decomposition and reaction behavior of DPB and DEB getter molecules was investigated. Headspace analysis of the these compounds in the presence of carbon supported Pd catalyst shows that some amount of degradation occurs, leading to the formation of benzene.

An accurate quantitative profile of the headspace gases is required in order to determine the actual amount of decomposition of the getter compounds over time. Although SPME is a convenient technique for headspace sampling, it suffers gravely in that it does not

equally partition all species to which it is exposed, and so is inherently unquantitative. Quantification requires a calibration of partition coefficients for all known substances to which it is exposed. Direct gas sampling, or more aggressive adsorbents such as activated carbon, should be examined as alternatives that could provide a quantitative cross section of the headspace. This quantitative analysis in combination with closer observation of the material decomposition over time and temperature can give kinetic and thermodynamic information relevant for making predictions about the getter stability in deployment.

For samples of both DPB and DEB getter, it was shown that a loss of capacity of about 15 to 20% can be induced by reacting the materials at low rates. A hypothetical mechanism for this loss was proposed based on time-dependent reaction data. These data indicated that capacity loss is due to an underlying requirement that as getter is consumed close to the catalyst surface, new getter must diffuse toward the catalyst to sustain the reaction. Thus, the ultimate capacity can be attributed to the thermal history of the material during the course of reaction, since the diffusion will be a function of available heat. TEM results supported this picture by revealing that some fraction of the Pd particles on the carbon surface are separated by large distances. Consequently, the lost capacity is probably related to the amount of getter material that is in the intervening space between catalyst particles, and which is too far from a catalyst surface to diffuse to it on the time scale of the experiments.

The loss of capacity of the getter is seen to be a function of both the level of getter consumption and the ambient hydrogen pressure. Beyond intermediate consumption (typically 40%), the getter capacity effectively becomes zero for low, though non-negligible hydrogen pressures, generally of about 1 Torr, at room temperature. As the getter is further consumed, the background pressure at which no reaction occurs increases. It is possible for the getter to continue to react provided the pressure is raised above background.

The main questions for further study based on the these results are:

1) Does getter diffusion truly control the reaction, and if so, what are the getter diffusion kinetics?

2) What role does liquefaction of the getter material play in the mechanism in terms of both obstruction of gas access and transport of unreacted getter?

3) What is the temperature dependence of the getter capacity?

4) What are the quantitative amounts of benzene and other components produced by getter decomposition, and what are the decomposition kinetics?

5) How does the volatility of the getter reaction products affect the ultimate capacity?

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